Petroleum and Coal

Article **Open Access**

DESIGN, CONSTRUCTION AND PERFORMANCE RELIABILITY VERIFICATION EVALUATION OF A HIGH PRESSURE VOLUMETRIC SORPTION SYSTEM FOR CO_2 SORPTION IN SOUTH AFRICAN COALS

K. Premlall[1], M. M. Mabuza[2], and J. H. Potgieter[3]

[1] *Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa*
[2] *Department of Chemical Engineering, Vaal University of Technology, Secunda, South Africa*
[3] *School of Chemical and Metallurgical Engineering, University of Witwatersrand, Johannesburg, South Africa*

Received May 5, 2019; Accepted July 15, 2019

Abstract

High pressure sorption equipment are based on the gravimetric or volumetric principle method of gas sorption onto a specific sorbent. This paper discusses the design, construction and performance consistency testing that was conducted on a recently constructed in-house high pressure volumetric sorption system (HPVSS) in South Africa (SA) which was used for the evaluation of supercritical carbon dioxide (CO_2) sorption on SA coals. A detailed description of the equipment, the commissioning phase, leak testing evaluation, estimation of sample, reference and void volume, as well as the method of conducting the measurements of the sorption isotherms are explained.

Six (6) South African (SA) coals were selected based on their myriad of properties i.e. coal rank, coal type, and petrographic and proximate analyses. The samples were used as the sorbing material for pure CO_2 in supercritical phase to conduct the isothermal sorption investigations. In order to evaluate the system, multiple reliability experimental runs were conducted and the isotherms were evaluated and the sorption data was verified using the one-way analysis of variance method (ANOVA) to ensure the equipment performance was statistically reliable. Both the, system temperature and pressures, were varied to determine the potential risks of leaks in order to validate the consistency of the system at varying conditions of supercritical gas injection.

For the total number of experimental test runs that were conducted, was observed that very good repeatability of the sorption data was reproduced under all conditions. The data exhibited good homogenous variance in all data sets compared, thus demonstrating overall confidence in the repeatability of these CO_2 results, and that the reliability of the HPVSS has been confirmed in the test sorption experiments. A comparison to both national and international published data sets also confirmed good fit of the findings.

Keywords: *Sorption of super-critical CO_2; Volumetric system; High pressure; Coal, Design validation; Repeatability investigations.*

1. Introduction

The awareness of, and the issues relating to climate change has become more evident in recent decades. These are reflected by increases in global temperature leading to severe droughts, hurricanes, typhoons, etc. and an increase in global sea mean level (GSML) [1]. The increase in greenhouse gases (GHG's) over the last few decades, especially for anthropogenic carbon dioxide (CO_2), from the burning of fossil fuels for energy, is reportedly responsible for climate change. The latest atmospheric CO_2 measurement recorded for August 2018 stands at 409 parts per million (ppm) compared to the recording from 2005 which was at 378 ppm [2]. According to the stipulated 2°C increase limit as outlined as at the COP 21 (December 2015) Paris Agreement held by the United Nations Framework Convention on Climate Change (UN-FCCC) at which a 195 countries, including South Africa (SA) agreed upon, it was declared that

urgent reform in mitigating CO_2 emissions must be implemented with immediate effect. Thereafter, following COP 22 held in Marrakesh (November 2016), it was finalized that further decisions relating to the "global stocktake" process looking at long term goals, market mechanisms and implementation relating to timelines, duration and output for individual country compliance to GHG emissions will be reviewed at the next COP 24 to be held in Poland in November 2018 [3].

Despite being a developing country, SA has been ranked as one of the top 15 emitters of CO_2 in the world [4]. Due to the South African economy's high carbon intensity and hence high CO2 emissions, it must be assumed that pressures on SA to reduce emissions can only increase. The country has committed itself to a low carbon emission future and in doing so launched SA's White paper on Climate Change [5] confirming to engage in all aspects to reduce and to mitigate CO_2 emissions. Three key elements have been identified: is a long term goal in the form of national emissions trajectory range to 2050: 2), is a medium term goal which will be within the range of 398 – 614 Mt of CO_2 equivalent in the years from 2025 and 2030; and 3), to provide periodic reviews in the medium/longer term to try and align to meet the 2°C target [5].

Carbon capture and storage (CCS) technologies are one of the integral aspects of the Intergovernmental Panel on Global Climate Change [6]. With the need to reduce the current SA emissions in line with the mandatory requirements, as outlined, that motivated the current research into evaluating the potential for the sorption capacity of CO_2, for emission reduction purposes, in unmineable SA coals. This will have the additional benefit of potentially enhancing methane (CH_4) recovery for use as an energy alternative, whilst also sequestering CO_2 emissions from large industrial point sources to establish a low carbon emission economy is anticipated. The research work seeks to develop key knowledge understanding of the sorption potential of SA coals. This work follows on from investigations and findings from the Carbon Capture Centre for Capture and Storage (SACCCS). After investigations and the subsequent publication of the SA Atlas [7], it was established that an overall storage capacity of 150 gigatons (Gt) (on-shore) was readily available relating to CO_2 storage capacity of approximately 1 271.9 million tonnes (Mt) [7-8].

In order to conduct such work relating to establishing sorption capacity at high injection pressures of CO_2 into SA coal, our research investigation required the need of a high pressure sorption system to undertake the necessary CO_2 sorption evaluations for capacity estimation of a myriad of SA coal types. This led to the need to design and construct a system that could be effective in generating research data to validate the SA coals sorption capacity and assess the potential for sequestration.

2. Design of the high pressure volumetric sorption equipment

In order to achieve the required high pressures of CO_2 needed for in-situ (underground) storage conditions during injection (supercritical gas state), a high-pressure volumetric sorption system was designed in order to conduct experiments to produce CO_2 sorption isotherms in order to estimate the maximum sorption capacities of the six (6) different SA coal types under investigation. There are many factors that influence the choice of sorption system (volumetric or gravimetric) to use for high-pressure sorption experiments. These include, but are not limited to: cost time of construction, accuracy, availability of material, and maintenance. In literature it has been extensively documented that the volumetric sorption method has been proven to be the most widely used and effective technique for determining gas sorption capacities on coal by numerous researchers [9–28]. The setups are generally either custom made, or designed in-house, and consist typically of calibrated reference and sample reactor cells.

The current volumetric system (HPVSS) designed for use of these SA coals sorption capacity trial estimations was modelled and designed as per designs found in literature was constructed in-house at Tshwane University of Technology (TUT), SA. Chemvak cc (Applied Chemical and Vacuum Systems), Pretoria, South Africa, constructed and refined the design with TUT over a period of two and a half years. Equipment commissioning took three (3) months.

Since the HPVSS final modification and inception, there have been four (4) peer-reviewed journal publications [29–32] as well as five (5) peer-reviewed international and local conference [33–37] contributions based on the sorption experiments conducted using this equipment to verify the reliability of its operation and data generated from it. A summary of details to consolidate the equipment design, construction, commissioning and verification is provide in detail in this paper.

2.1. Equipment description

A simple schematic diagram of the in-house designed and constructed High-Pressure Volumetric Sorption System (HPVSS) is shown in Figure 1.

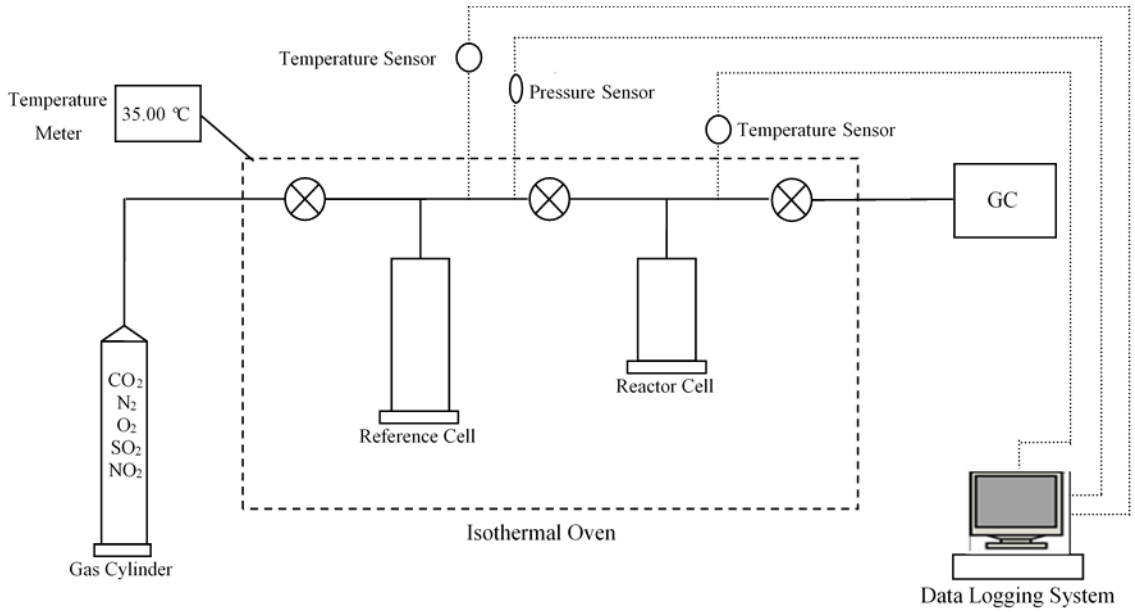

Figure 1. Simple schematic presentation of the high-pressure volumetric sorption system

The experimental setup consists of a reservoir cell (reference cell), a sorption / reactor cell (sample cell), and a digital control system for temperature and pressure control. The reservoir and sorption cells were manufactured of stainless steel and have volumes of 467.20 and 43.79 cm^3, respectively (after final modification). Maximum pressures of 15.0 MPa can be attained. The pressure in the reservoir and sorption cells was controlled and monitored by a digital control system connected to a WIKA pressure transducer (model A-10). A data logging system connected to the temperature and pressure transducers was used to collect the temperature and pressure data every second.

The interconnecting manifolds were made of stainless steel tubes and the valves were designed to withstand high pressures. However, these valves needed to be regularly replaced, depending on the frequency of use of the equipment, to prevent any gas leakages. Metallic (stainless steel) seals were used to join the various manifolds. They were selected based on the fluid used (either gas or super-critical) and the operational temperature (30–60ºC) and pressure (0–15.0 MPa).

A gas chromatograph (GC) (Model 8610), supplied by Chromspec chromatography is connected to the HPVSS experimental setup by a 1/8 in. stainless steel tube (Figure 1). Most importantly, proper calibration of the GC was essential; if not done frequently and correctly, the resulting sorption results will not be reliable. During the GC commissioning, the GC was calibrated by the supplier (Afrox Pty Ltd) using pure gases. This procedure was repeated performed on a quarterly basis.

The comprehensive HPVSS diagram is presented Figure 2 in which details of each component in the equipment are described. The supplier equipment details are outlined in Table 1.

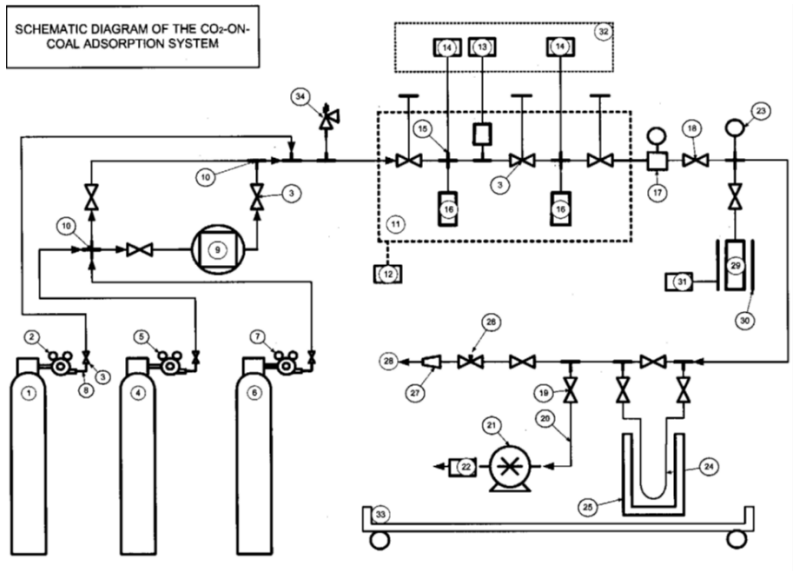

Figure 2. Detailed schematic diagram of high-pressure volumetric sorption system

Table 1. Components descriptions of the HPVSS

No.	Component	Supplier	No.	Component	Supplier
1	N2 gas cylinder	Afrox	18	SS ¼" shut-off valves	Chemvak
2	N2 pressure regulator	Afrox	19	NW 16 vacuum valve	Chemvak
3	¼" SS bellows seal valves	Chemvak	20	NW 16 vacuum line + couplings + O-rings + clamps	Chemvak
4	CO2 cylinder	Afrox	21	2 m3/h sliding vane fore-vacuum pump	Chemvak
5	CO2 pressure regulator	Afrox	22	Outlet oil mist trap	Chemvak
6	Flue gas cylinder	Afrox	23	Mechanical vacuum gauge	Chemvak
7	Flue gas pressure regulator	Afrox	24	U-tube volatiles trap	Chemvak
8	¼" SS tubing	Chemvak	25	Liquid N2 dewar (small)	Chemvak
9	Compressor	Chemvak	26	SS ¼" Needle valve	Chemvak
10	Swagelok ¼" SS unions	Chemvak	27	SS reducer to GC	Chemvak
11	Used GC oven	Chemvak	28	Gas chromatograph	Chromspec
12	Temperature control and Power Supply	Chemvak	29	Clamp-on heater	Chemvak
13	0-200 bar pressure transducer + digital readout + PS (Model A-10)	WIKA	30	Clamp-on heater	Chemvak
14	Thermocouple (2) + digital readout + switch	Chemvak	31	Temperature controller (basic) + Thermocouple + PS	Chemvak
15	Thermocouple SS couplings	Chemvak	32	Instrument panel	Chemvak
16	Reference and Sample Cells	Chemvak	33	Trolley	Chemvak
17	Single-stage, in-line pressure regulator + couplings	Chemvak	34	Pressure release valve	Chemvak

Figure 3 shows the actual HPVSS that was constructed and tested using the six (6) SA coals in –house at TUT, SA. Figure 3(a) shows a picture of the total designed equipment, while Figure 3(b) shows a picture the internals of the HPVSS.

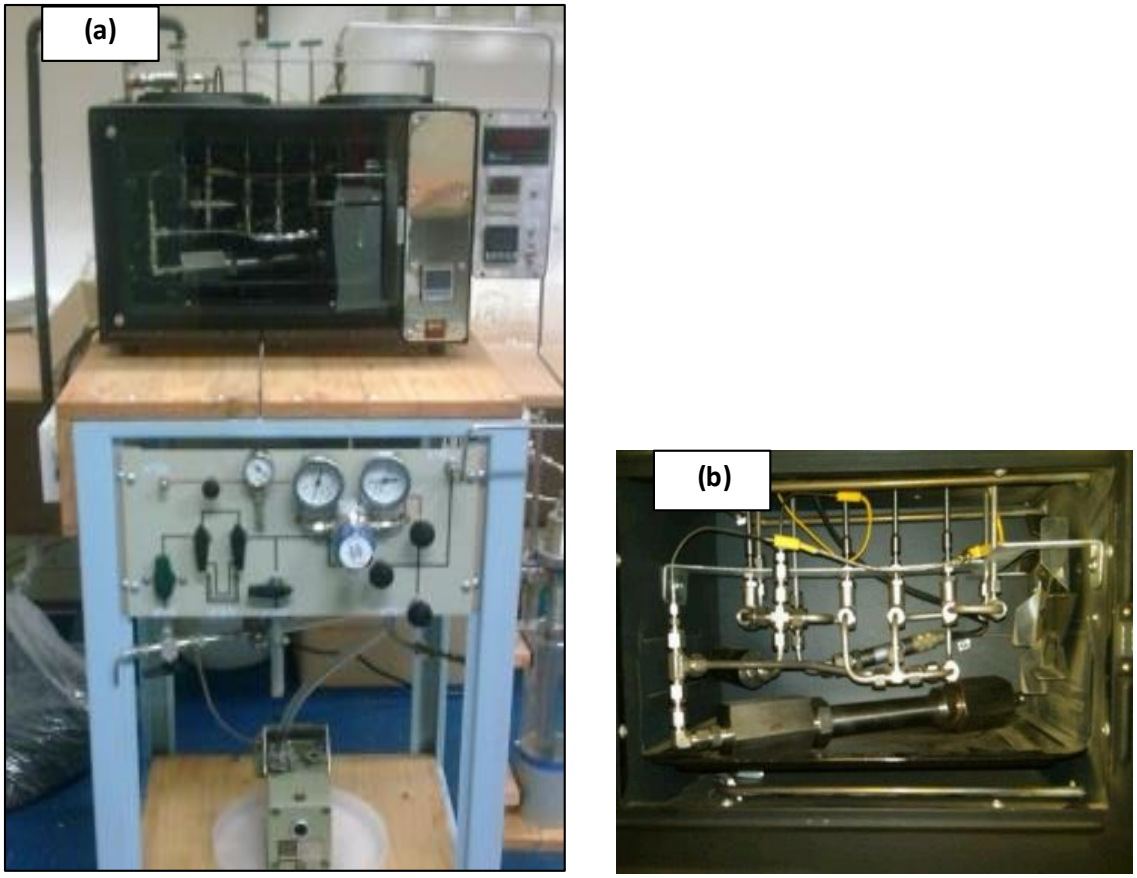

Figure 3. (a). Picture detailing the High-Pressure Volumetric Sorption System; 3(b). System internals

2.2. Equipment commissioning

2.2.1. Leak test

Due to the small volumes and high-pressures associated with the experimental setup, a leakage test was necessary to certify a hermetic seal of the entire equipment. This test was performed by introducing helium to the system at a pressure of 0.9 MPa with using incremental temperature from 35 to 60ºC. These temperatures and final pressure were selected based on the desired maximum sorption conditions. The pressure was monitored and recorded continuously at constant temperatures for 48 hours. Any leakage occurrences were detected by a decline in the system pressure with time. An Afrox Safetest Leak Detection Solution was applied to the pressurized connections. Formation of bubbles suggested a leakage, and, thus, the connections were tightened and fixed accordingly. In case the Swagelok connections were worn due to cross-threading or any other possible reasons, they were immediately replaced before any tests were conducted.

2.3. Determination of the reference and sample cells volumes

The use of a volumetric system requires accurate measurements of the reference and sample cells volumes. Hence, this procedure was central during the commissioning of this HPVSS equipment [14-15, 20, 22, 38-39]. Initially, the empty volumes were evacuated using a vacuum pump. The volumes were determined by a series of helium expansions from the reference cell to the sample cell. The expansions were carried out at low helium pressures (0.1, 0.2, 0.3 and 0.4 MPa) and at a room temperature of 25ºC. The assumption was that helium acts as an ideal gas under these conditions; thus, the ideal gas law equation was used for calculations. Furthermore, an additional cell of known volume was required to aid in determining these cells' volumes. After this procedure, the additional cell was disconnected from the system

since it was not necessary during to sorption experiments. The detailed procedure and equations governing the estimation of these volumes are described in detail by Mabuza [40].

3. Measurement of sorption isotherms

3.1. Sample degassing and moisture equilibrating

The sorption capacity and other properties such as the coal density, pore size, surface area, and porosity of the coals could be affected by the presence of moisture within the coal sample [41-42], other elucidations cannot be precluded entirely; however, residual moisture seems to play the most dominant role in affecting the sorption capacity on coals [42-43]. Each coal sample was degassed and dried before the sorption measurements were conducted. A sample mass in excess of 10 g (to account for the mass reduction after degassing) was weighed and placed in the HPVSS sample preparation cell and clamped on the heating element (component 29 in Figure 2). The sample was evacuated (- 0.7 bar) at a temperature of 120ºC for a maximum period of 2 hours. Thereafter, the samples were moisture equilibrated to 4% using distilled water prior the sorption experiments. The moisture content of 4% was chosen based on the average moisture content of the coals under investigation. A UniBloc Moisture Analyzer (Mode MOC63u) was used to accurately measure the coal moisture content.

3.2. Placement of the coal sample in the sample cell

After degassing and moisture equilibrating the sample, the sample was pre-weighed to get a prescribed amount of 10 g and was placed inside the sample cell. The sample cell was thoroughly tightened secured in its place. The sample was placed under vacuum for 60 s; thereafter, the system was leak tested using helium [45].

3.3. Measurement of sorption isotherms

3.3.1. Estimation of the void volume in the sample ell

Before sorption isotherms measurements, by the introduction of the sorbate gas (CO_2 or flue gas) into the sample cell could commence, the void volume (V_{void}) was estimated using the helium expansion approach. This approach is similar to the one applied in section 2.2. According to Ozdemir [39] the V_{void} is the available volume in gas-phase in the sample cell, Krooss *et al*. [14] simplified the description of V_{void} by referring to it as the volume not occupied by the solid sample as shown in Figure 4. It should be noted that V_{void} is dependent on the sample volume; thus, one can obtain a different value for the same material unless the mass consistently remains unchanged.

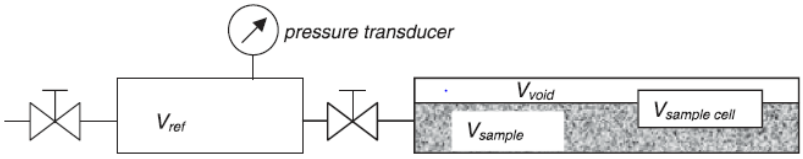

Figure 4. Focused area of the HPVSS showing the definitions for the volumetric method [15-16]

The detailed procedure and equations governing the estimation of the void volume are described and discussed as follows using Figure 5 which shows a simplified diagram of the HPVSS.

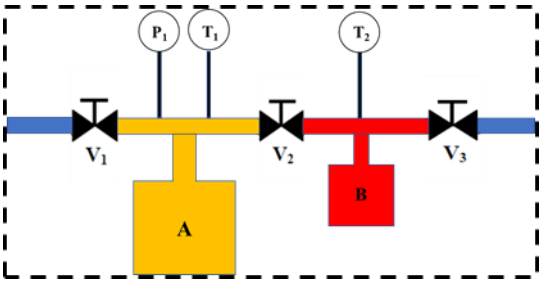

Figure 5. Simplified HPVSS diagram with the reference and sample cells volumes (without the standard cell)

The experimental procedure was as follows:

1. The system was evacuated using a vacuum pump with valves V_2 and V_3 open, and valves V_1 closed.
2. All valves were closed after 60 seconds of evacuation.
3. Helium was introduced into the reference cell, V_A, with valve V_1 open. The displayed pressure P was recorded as P_i.
4. Valve V_1 was closed and helium was allowed to expand to the sample cell, V_B, by opening valve V_2. The displayed pressure was recorded as P_f. Following the approach by Sudibandriyo [45] and the expressions that govern the approach, the recorded data was used as follows:

$$V_{void} = n_{He}\left(\frac{z_{He}RT}{P}\right) \quad (1)$$

where number of moles of helium introduced into the cell is:

$$n_{He} = \frac{V}{RT}\left(\frac{P_i}{z_{He,i}} - \frac{P_f}{z_{He,f}}\right) \quad (2)$$

where: V is the volume of the dozing cylinder; P_f and P_i represent final and initial pressure of that cylinder respectively; R is universal gas constant and *z* is the compressibility factor.

The helium compressibility factor was evaluated using the Peng-Robinson equation of state. The helium compressibility factor is given by:

$$z_{He} = 1 + \frac{\left(1.471\times10^{-3} - 4.779\times10^{-6}T + 4.92\times10^{-9}T^2\right)}{P} \quad (3)$$

where P is in atmosphere and T is in Kelvins.

This expression is based on the experimental data from National Bureau of Standards Technical Note 631 for helium [46]. The same procedure was repeated for pressures up to 0.9 MPa.

3.3.1. Estimation of sample volume

The sample volume determination is essential for calculation purposes in the measurement of sorption isotherms. The following expression has been successfully applied by Busch *et al.* [16] to determine the sample volume and had since been adopted in the current research:

$$V_{sample.Cell} = V_{sample} + V_{void} \quad (4)$$

Knowing $V_{sample.Cell}$ obtained from section 2.2 and V_{void} obtained from section 3.3.1 allows the, V_{sample} to be determined as follows:

$$V_{sample} = V_{sample.Cell} - V_{void} \quad (5)$$

The gas phase specific density is significantly lower than that of the adsorbed phase and the volume of the latter can be neglected. In this case, the evaluation scheme results in the so called "excess sorption" or Gibbs sorption [13, 17].

3.1.2. Estimation of sample density

According to Hidnert and Peffer [47], the density of a solid having a fixed geometrical form may be reasonably estimated by a volumetric approach with an error of about 1 percent. This estimation can be performed using the following expression:

$$\rho_s = \frac{m_s}{V_s} \quad (6)$$

where ρ_s is the sample density; m_s is the sample mass, and V_s is the volume of the sample inside the sample cell.

The sample mass may be conveniently obtained using a balance, accurate to 3 decimal figures, prior to placing the sample inside the sample cell. Thus, knowing V_s from Equation 5 and m_s from Section 3.2, the estimated value of the coal sample density may, then, be computed. The density value acquired through the use of Equation 6 was validated using a helium Stereopycnometer. Details of coal densities for these SA coals are summarized in Table 3. Details of the use of a helium Stereopycnometer, as well as the equations that govern its use, are presented and described fully by Mabuza [40].

Table 2. Experimental conditions for pure CO_2 sorption isotherm measurements

Experimental conditions	Coal samples					
	AN	IN	SF	GS	EM	SM
Temperature (ºC)	35	35	35	35	35; 50; 60	50, 60
Average sample mass (g)	5.04	5.05	5.04	5.01	5.05; 9.96; 10.0	9.68; 10.01
Average sample density (g/cm^3)	1.59	1.47	1.59	1.64	1.84	2.02
Average void volume (cm^3)	61.75	61.46	61.75	61.48	61.81; 38.33; 38.38	38.75; 38.82
System Pressure (MPa)	<.....1.0 – 9.0 --..... ...>					
Incremental pressure steps	9	9	9	9	9	9
Gas composition (mol%)	99.999 CO_2	99.999 CO_2	99.999 CO_2	99.999 CO_2	99.999 CO_2	99.999 CO_2
Fluid state	Gaseous to supercritical					

Table 3. Proximate, ultimate and petrographic data of SA coals tested

Sample ID:	***AN***		***SM***		***SF***		***GS***		***IN***		***EM***	
	db	*daf*	*db*	*daf*	*db*	*daf*	*db*	*daf*	*db*	*daf*	*db*	*daf*
PROXIMATE												
Moisture %	1.4		1.1		5.0		3.4		2.0		4.5	
Vol. matter %	5.2	5.7	7.7	9.9	24.3	30.1	32.3	36.0	23.3	28.6	39.0	47.5
Ash %	8.8	9.6	18.2	22.2	19.3	23.9	10.3	11.5	18.4	22.5	17.9	21.9
Fixed C %	84.6	92.8	72.9	89.1	51.4	63.7	53.9	60.1	56.3	69.0	27.8	33.9
ULTIMATE												
Sample ID:	***AN***		***SM***		***SF***		***GN***		***IN***		***EM***	
C %	82.0	89.9	73.7	90.1	59.5	73.7	69.8	77.8	66.8	81.9	60.3	73.5
H %	3.1	3.4	3.3	4.1	3.7	4.6	4.9	5.5	4.0	4.9	3.7	4.5
N %	1.9	2.1	1.6	2.0	1.5	1.9	1.8	2.0	1.6	1.9	1.5	1.9
O%	3.3	3.7	2.5	3.1	14.5	18.0	12.7	14.2	8.3	10.2	15.9	19.4
S %	0.9	1.0	0.6	0.8	1.4	1.8	0.5	0.5	0.9	1.1	0.5	0.6
Total	100.0		100.0		100.0		100.0		100.0		100.0	
PETROGRAPHIC DATA												
Sample ID:	***AN***		***SM***		***SF***		***GN***		***IN***		***EM***	
Vitrinite vol%[a]	33.4		88		20.8		51.4		50.2		13.9	
Inertinite vol%[a]	66.6		12		76.7		43.9		47.3		82.2	
Liptinite vol%[a]	0		0		2.5		4.7		2.5		3.6	
Mineral Mat. vol%	4.6		4.5		12.4		11.2		10.4		9.8	
R_oV_{mr} vol%[b]	2.91		2.24		0.65		0.7		0.81		0.64	
Coal Rank	***HRC***		***HRC***		***MRC***		***MRC***		***MRC***		***MRC***	
Density (g/cm^3)	1.59		1.8		1.59		1.48		1.47		1.64	

3.3.4. Construction of sorption isotherms

3.3.4.1. Pure gas (CO_2) sorption isotherms

Sorption isotherms and sorption capacities for pure CO_2 on the selected six (6) South African coal samples were measured under simulated in-seam conditions. This included pressures up to 9.0 MPa and isothermal temperatures ranging from 35ºC for five of the different coals and up to 50 and 60ºC for two other coal types. The experimental conditions are presented in Table 2. Table 3 details the proximate, ultimate and petrographic data of the selected coals that were tested during this investigation.

Three repeatability CO_2 sorption tests were conducted on the first coal type, AN at 35°C. Thereafter two repeats per rest for the four coal types were done to ensure reproducibility. Judgements were based on visual observations of the sorption isotherms. After this, a small modification was done to the system to reduce the reactor cell volume which lead to a reduction in void volumes. It was thereafter, that the temperatures for tests on the two selected coal types, EM and SM were changed and test runs were done for temperatures of 50 and 60°C. Three (3) sorption trials were performed due to the nature of deviations that could occur for higher temperatures, as outlined by Oldenburg, Charriére *et al.,* and Qing-Ling *et al.* [48–50].

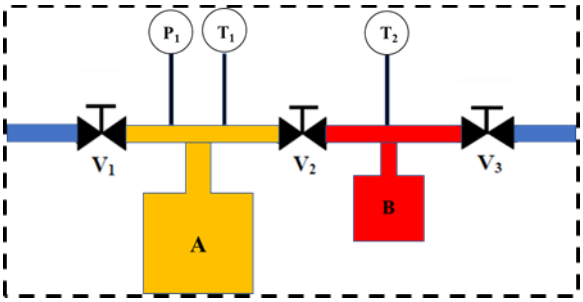

Figure 6: Simplified HPVSS Diagram for Determining the Reference and Sample Cells Volumes (without the standard cell)

To generate isotherms, the following procedure, with reference to 3 and Figure 6, was followed:

- The system oven was switched on and set to a desired temperature, as per the experimental conditions in Table 2. To achieve thermal equilibrium, at least 15 minutes were allowed in the system oven. However, during the initial thermal stability tests of up to 30 minutes it was confirmed that 10 minutes was sufficient to reach thermal equilibrium for these specific mass of coal samples used.
- The system was then evacuated using a vacuum pump with valves V_2 and V_3 open. The reference cell was charged with CO_2 gas to desired pressure by opening valve V_1, with valves V_2 and V_3 closed. Valve V_1 was closed to separate the reference cell from the CO_2 gas cylinder. Up to 5 minutes were allowed for the pressure in the reference cell to stabilize; in some instances, this pressure stability was achieved in much lesser time.
- The computer data logger was initialized to start recording the pressure and temperature of the sorption experimental run.
- The gas in the reference cell was, then, expanded to the sample cell by opening valve V_2. The pressure of the system was closely monitored until equilibrium was reached. In the initial (trial) tests run up to 24 hours. However, it was found that, 90 minutes was adequate for the equilibrium point to be reached.
- The same procedure was repeated for eight more pressure steps up to the final pressure of 9.0 MPa as shown in Figure 7.

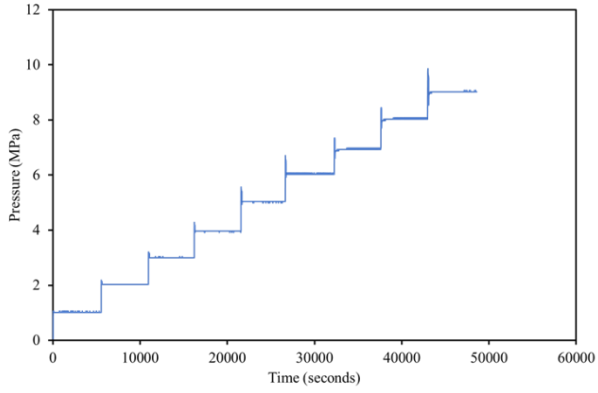

Figure 7. Sorption experimental pressure steps

The most fundamental operational procedure to quantify gas sorption on solid surfaces is the Gibbs approach. With this approach, the amount of gas sorbed (n_{sorbed}) is defined as the difference between the total amount gas (n_{total}) present in the system and the amount occupying the void volume (V_{void}), i.e. the volume unoccupied by the solid sample. According to Krooss *et al.* [14] the Gibbs approach as mathematically described in Equation 7, assumes a constant ratio of condensed phase volume and void volume throughout the sorption experiments and requires no further assumptions. The initial and equilibrium pressure molar densities of the gas phase were determined using data acquired from the National Institute of Standards and Technology WebBook (NIST) database [51]. The NIST Chemistry WebBook uses the Span

and Wagner [5] equation of state for CO_2 covering the fluid region from the triple-point temperature to 826.85ºC at pressures up to 800 MPa. Details of the equations applied in the calculation of the CO_2 fluid sorbed on the coal surface are described in Mabuza [40].

The Gibbs approach was used to calculate the amount of CO_2 sorbed. This approach is based on the mass balance between the sample cell and the reference cell for each pressure expansion step. The Gibbs approach is based on the following expression:

$$n_{sorbed}^{excess} = \frac{n_{total} - \rho_{eq} V_{void}}{m_s} \quad (7)$$

Furthermore, the amount of gas adsorbed was expressed in the absolute form in Equation 8.

$$n_{sorbed}^{absolute} = \frac{n_{sorbed}^{excess}}{1 - {}^{\rho_{gas}}/_{\rho_{ad}}} \quad (8)$$

where n_{sorbed}^{excess} is the absolute adsorbed amount of CO_2 (mmol/g); $\rho_{adsorbed}$ is the gas adsorbed phase density (in this case CO_2) (mmol/cm^3).

The adsorbed phase density is usually assumed to be constant across the experimental range [52]. In this study the value of 22.6 mmol/cm^3 for CO_2 was adopted since it has been found to be a reasonable estimation and was previously successfully applied by numerous other authors [43-44, 48, 53]. The adsorbed-phase density estimates do, however, affect the calculated absolute adsorption isotherm [45].

3.3.5. Data analysis methods

3.3.5.1. Analysis of variance (ANOVA)

The experimental CO_2 sorption data generated using the HPVSS for all repeat tests runs for the different SA coal types and at the different temperatures (35, 50 and 60°C) was analysed for variance (determination of repeatability) using a one way ANOVA method available in the data tool pack (add-in) in Microsoft Excel. It is a non-parametric method that is most recommended to be used in comparing two or more groups of sorption sample data in order to determine inequality in the data sets and is a hypothesis test with the F statistic (ratio of two quantities) which was used to test the null and alternative hypotheses. Specifically, it tests the null hypothesis:

$$H_o: \mu_1 = \mu_2 = \mu_3 = \cdots = \mu_k \quad (9)$$

where μ = group mean and k = number of groups.

This means that "There is *not* a significant difference between the groups; any observed differences may be due to chance and sampling error". This is realised from the computed data key criteria, i.e the F statistic value must be less than the calculated F critical value. Furthermore, the P value computed must be greater than 0.05 which is the smallest level of significance [54].

4. Results and discussions

4.1. Leakage tests

Due to the nature of high pressure work and the reliability of results needed for the sorption by pressure difference calculations, the system was subjected to a number of leak tests. Five (5) South African bituminous coal (same coal) samples were subjected to pressure for a number of days (Figure 8). Some of the tests were stopped at different intervals (for some of the trial tests) due to testing, modification requirements, and installation of a new automated data logging system. This was also necessary due to the long adsorption test times noted. Results below are indicative of manual pressure and time recordings.

As seen in Figure 9, a good comparison for trial runs for tests 2, 3, and 5 showed evidence of good repeatability for a specific SA bituminous coal type. This was considered to be an

acceptable starting point for further test work, and eliminated concerns regarding system leaks at CO_2 super-critical conditions.

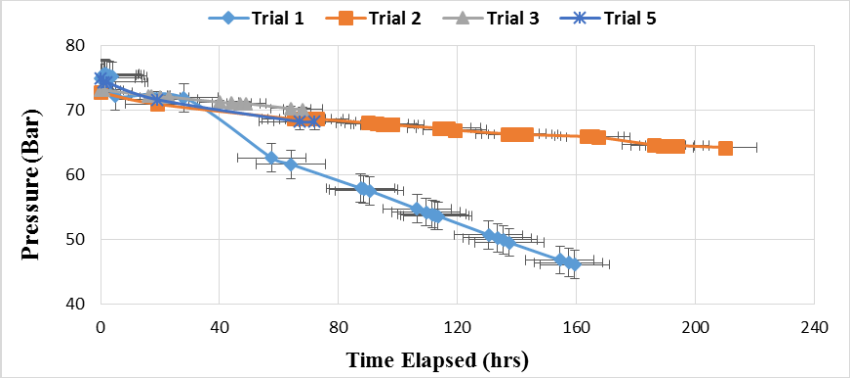

Figure 8. CO_2 injection pressure leakage tests

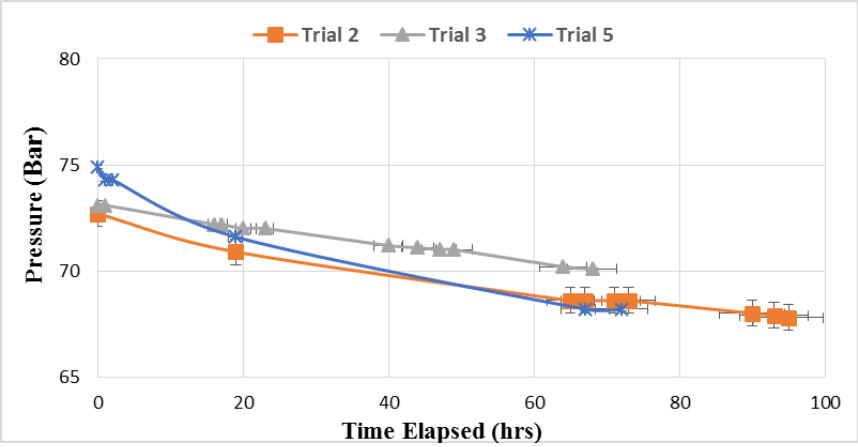

Figure 9. Three repeatability trial tests
Trial 2 run for 67.8 hrs ~ 3 days; Trial 3 run for 68 hrs = ~ 3 days; Trial 5 run for 72hrs = ~ 3 days

After inclusion of the data logging system, further leak tests were conducted. The adsorption system was again also checked for leaks to ensure that there were no pressure drops inside the reactor as this would influence the CO_2 adsorption results.

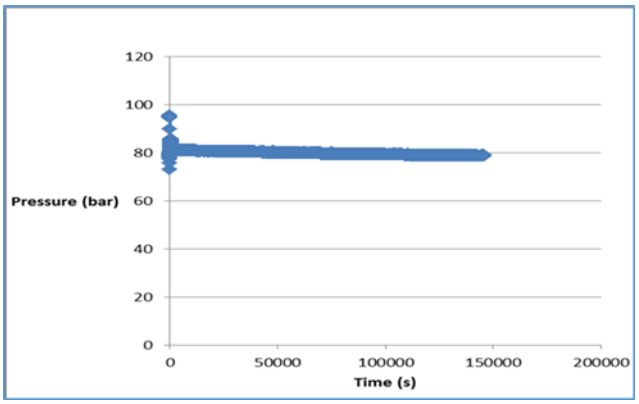

Figure 10. Leak test results on adsorption data logging system

The leak test was done by conducting a blank experiment where the pressure in the empty reactor was raised to approximately 98 bars, then the equipment was left overnight (12 hours or longer). It was expected that due to the temperature drops at night a slight pressure drop of small magnitude would take place. A significantly large pressure drop would indicate leakages in the system, possibly around the pipe fittings and valves. The final results of the leak test on the HPVSS are presented in Figure 10.

From the data logged results of leak tests undertaken, an insignificant pressure drop was experienced (Figure 9). This confirmed that the CO_2 sorption data acquired gave confident

results presented hence forth. Individual coals were then repeatedly tested to obtain the individual coal CO_2 sorption isotherms shown in section 4.2.

4.2. Sorption isotherms conducted at 35°C

To evaluate the repeatability of the HPVSS, five (5) different SA coal types were tested using the incremental pressure step to a maximum of approximately 9 Mbar. Figures 11, 12 and 13 illustrate the individual repeat test sorption isotherms for these coals. Coal AN's CO_2 sorption capacity was tested using three trial runs, thereafter the other four coals; EM, GS, IN and SF, were repeat tested twice. For each sorption test a fresh coal sample was prepared and used under the same experimental conditions of temperature (35°C) and pressure up to 9 Mbar. The mean ($\bar{x}$) total sorption capacity of each individual coal sample was then computed from the repeat data. The mean value, as well as the standard deviation (SD), is shown in Figure 13 and summarized in Table 4.

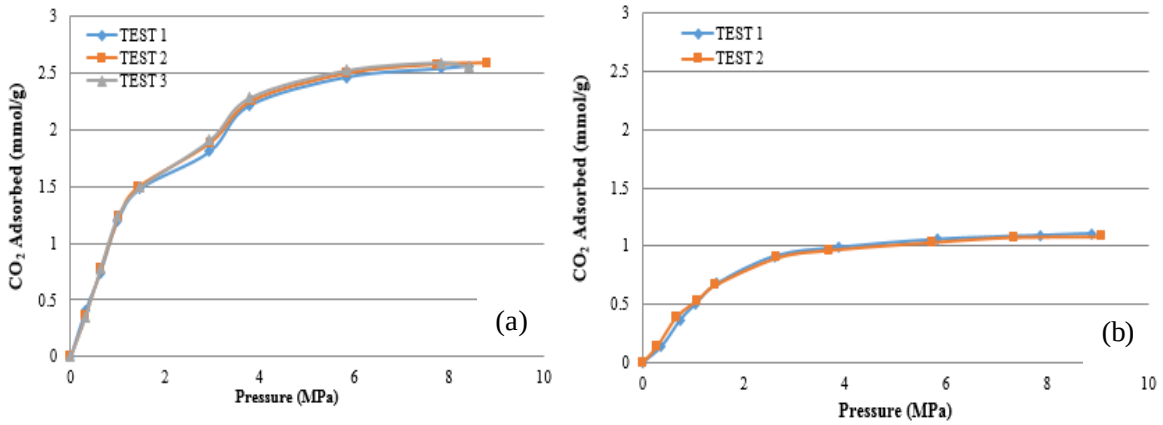

Figure 11. Adsorption Isotherms @ 35°C – (a) coal AN and (b) Coal EM

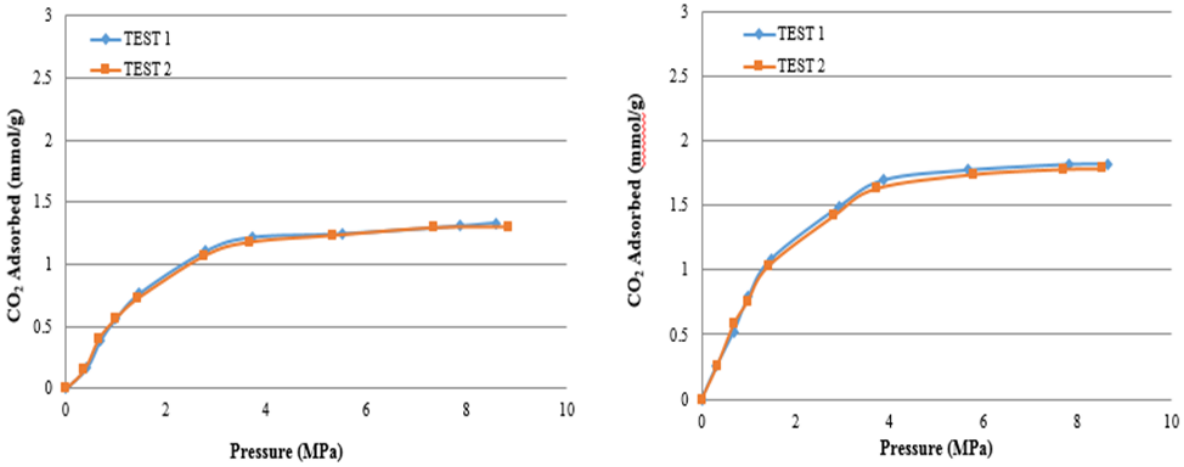

Figure 12. Adsorption Isotherms @ 35°C – (a) coal GS and (b) Coal IN

Sorption capacity isotherms for all coal types and the repeat tests increased monotonously from low to sub-critical pressures and exhibits an asymptotic behavior at high pressures (~ 6 MPa). From visual observations, it is quite obvious that a very good reproducibility of sorption results has been obtained for the repeat tests in all five of the coals tested. The differences in the measures (amounts) of CO_2 sorption capacities (mmol/g), as is clearly seen in Figure 14, is due to the nature of coal type and the details thereof informing this behavior will not be discussed in this paper. Only the validity of the specifically designed and constructed high

pressure volumetric sorption systems' ability to produce reliably repeatable results with homogenous variance will be focused on.

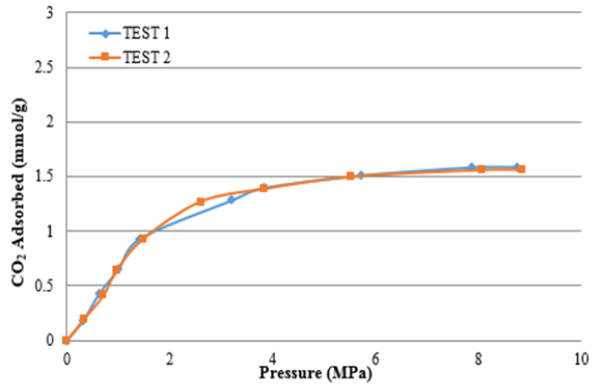

Figure 13. Adsorption Isotherms @ 35 °C – Coal SF

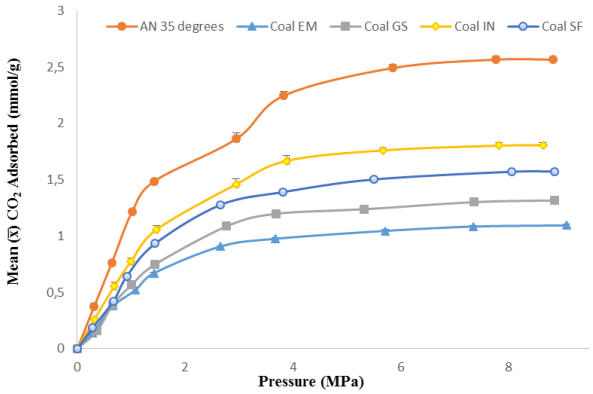

Figure 14: Average of repeat adsorption isotherms @ 35°C

Table 4. Summary of CO_2 sorption capacity data at 35°C

Sample ID and Test		Total sorption capacity (mmol/g)	Reference graph figure	Mean total sorption capacity ($\bar{x}$)	Sample Final Standard Deviation (SD)
Coal AN	TEST 1 TEST 2 TEST 3	2.56 2.58 2.55	Figure 10 (a)	2.56	0.02
Coal EM	TEST 1 TEST 2	1.10 1.08	Figure 10 (b)	1.09	0.014
Coal GS	TEST 1 TEST 2	1.33 1.30	Figure 11 (a)	1.32	0.02
Coal IN	TEST 1 TEST 2	1.82 1.79	Figure 11 (b)	1.81	0.02
Coal SF	TEST 1 TEST 2	1.59 1.56	Figure 12	1.57	0.02

4.3. Sorption isotherms conducted at 50°C and 60°C

To evaluate the equipment repeatability and sorption capacity reliability with respect to *increased experimental temperatures*, two (2) different SA coal types were tested using the same incremental pressure step to a maximum of approximately 9 Mbar at two temperatures, namely: 50°C and then 60°C [49-51]. Three (3) freshly prepared samples for each coal type for each sorption test were used. Figures 15 and 16 illustrates the experimental sorption isotherms for both these coal samples.

As was also noted in Section 4.2, sorption capacity isotherms for all coal types and the repeat tests can be seen to have increased monotonously from low to sub-critical pressures and exhibited an asymptotic behaviour at high pressures (~ 6 MPa). Visual inspection of the sorption isotherms, clearly imply that a good reproducibility of sorption data has been achieved. The mean ($\bar{x}$) total sorption capacity (mmol/g) of each samples was computed from the experimental repeat data, as well as the standard deviation (SD) and is summarized in Table 5.

Standard deviations computed for the coals tested at 50°C range from 0.061 – 0.068 and for temperature 60°C range from 0.021 – 0.027. The differences in these values are significantly small and show good repeatability was obtained for these test runs overall. The computed mean ($\bar{x}$) sorption isotherms depicting the average CO_2 sorption capacities (mmol/g) for both temperatures for the two tested coals, EM and SM, are illustrated in Figure 17 (a) and (b) respectively.

Table 5. Summary of CO_2 sorption capacity data at 50 and 60°C

Sample ID and test at 50°C		Total sorption capacity (mmol/g)	Reference graph figure	Mean total sorption capacity ($\bar{x}$)	Sample final standard deviation (SD)
Coal EM	TEST 1	2.77	Figure 14 (a)	2.84	0.07
	TEST 2	2.83			
	TEST 3	2.90			
Coal SM	TEST 1	2.92	Figure 14 (b)	2.93	0.06
	TEST 2	2.88			
	TEST 3	2.99			
Sample ID and test at 60°C		**Total sorption capacity (mmol/g)**	**Reference graph figure**	**Mean total sorption capacity ($\bar{x}$)**	**Sample final standard deviation (SD)**
Coal EM	TEST 1	2.25	Figure 15(a)	2.22	0.03
	TEST 2	2.22			
	TEST 3	2.19			
Coal SM	TEST 1	2.54	Figure 15 (b)	2.55	0.02
	TEST 2	2.57			
	TEST 3	2.53			

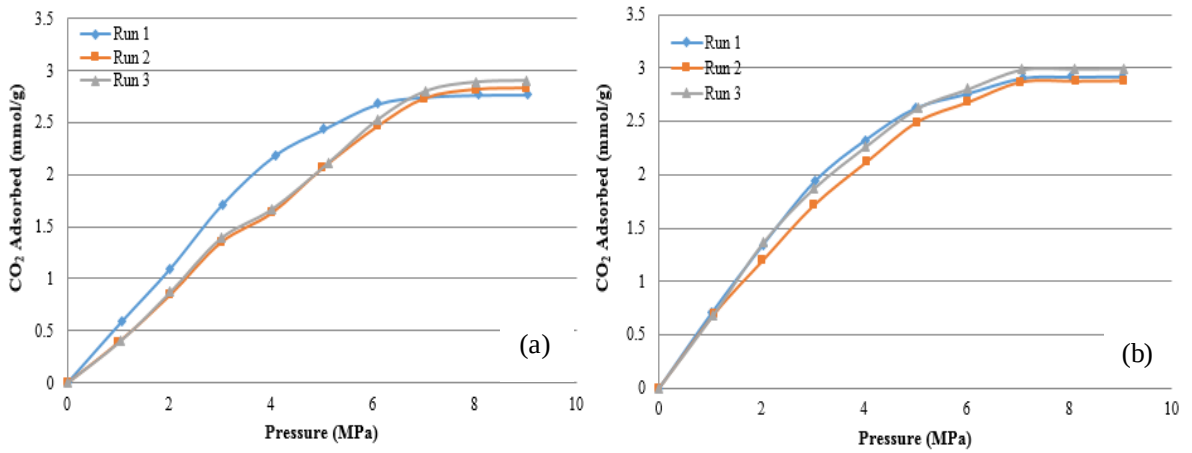

Figure 15. Adsorption Isotherms @ 50°C – (a) coal EM and (b) Coal SM

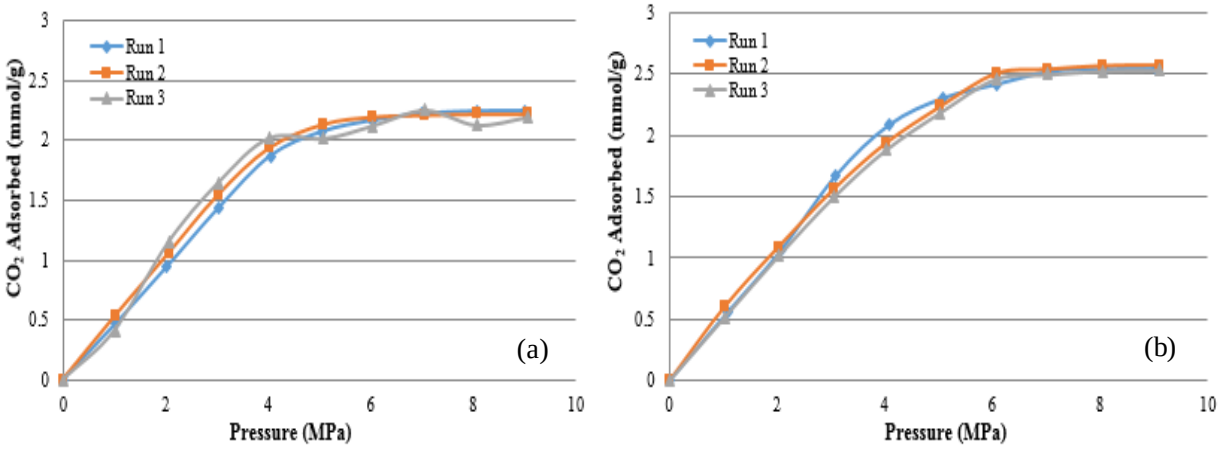

Figure 16. Adsorption Isotherms @ 60°C – (a) coal EM and (b) Coal SM

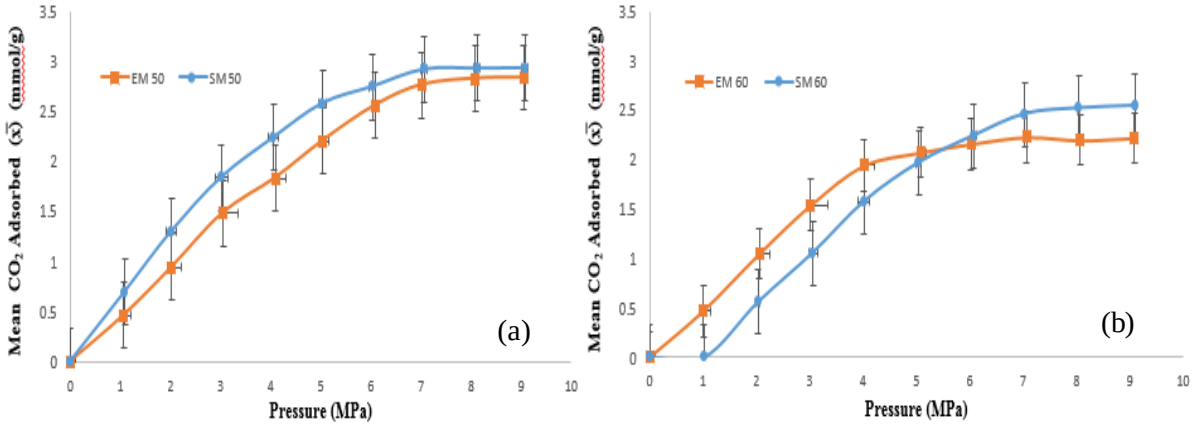

Figure 17. Average of Adsorption Isotherms @ 50 and 60°C

4.4. Analysis of Variance (ANOVA) results

The ANOVA statistical data was computed using Microsoft excel data tool pack, as detailed in Section 3.3.5.1 and was used to evaluate the potential of any variation of the experimental CO_2 sorption data set results. Results for the SA coals tested at experimental temperatures of 35°C, 50°C and 60°C are discussed in sections 4.4.1, 4.4.2 and 4.4.3 respectively. Tables 5, 6 and 7 summarize the statistical data showing results calculated for the sample sum (Σ), mean ($\bar{x}$), sample variance (s^2), standard deviation (SD), sum of squares (SS), degrees of freedom (d*f*), mean squared values (MS), F statistic (F), P-value and F critical values for each sample group, i.e. coal tested and repeat tested.

4.4.1 Coals tested at 35°C

Figure 18 illustrates the comparison of the five (5) SA coals tested at 35°C (coals AN, EM, GS, IN and SF) versus the computed mean sorption ($\bar{x}$) results in mmol/g per experimental coal sample. Error bars which represent the calculated standard deviation (SD) show that good repeatability can be observed for each coal type and test run conducted.

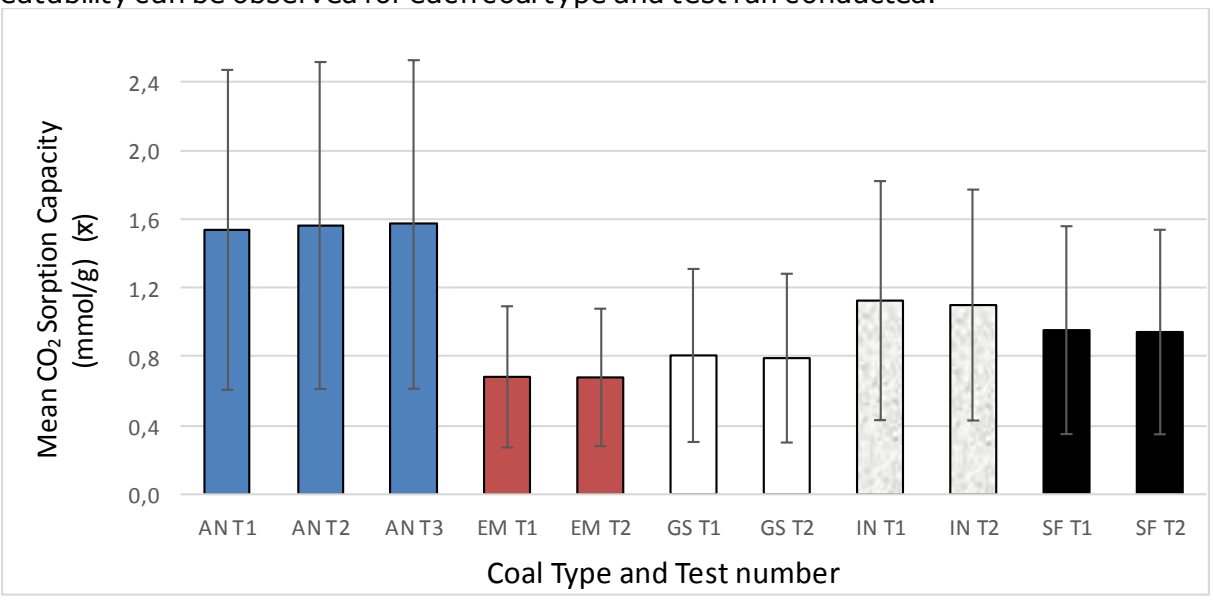

Figure 18. CO_2 sorption capacity comparison at 35°C using ANOVA results

Table 6 summarizes the statistical data computed. For all coals the F statistic values range in the region of 0.0 – 0.01, which is less than the computed F critical value range (3.35 –

4.41). This indicates an acceptable confidence level for repeat results obtained in this study. The p-values computed, range from 0.93 – 0.99, showing very good acceptable reproducibility of CO_2 sorption results from all these five SA coals tested. Therefore, the null hypothesis for these experiments is valid, i.e. there is *not* a significant difference between the groups or data sets.

Table 6. Data summary and ANOVA results of coals tested at 35°C

Summary data	*Test number*	*Count (n)*	*Sum (Σ)*	*Mean ($\bar{x}$)*	*Variance (s^2)*	*Standard deviation (SD)*
Coal AN	TEST 1	10	15.4	1.54	0.87	0.9
	TEST 2	10	15.6	1.56	0.90	1.0
	TEST 3	10	15.7	1.57	0.91	1.0
Coal EM	TEST 1	10	6.8	0.68	0.17	0.9
	TEST 2	10	6.8	0.68	0.16	0.4
Coal GS	TEST 1	10	8.1	0.81	0.25	0.5
	TEST 2	10	7.9	0.79	0.24	0.5
Coal IN	TEST 1	10	11.3	1.13	0.48	0.7
	TEST 2	10	11.0	1.10	0.45	0.7
Coal SF	TEST 1	10	9.6	0.96	0.37	0.6
	TEST 2	10	9.4	0.94	0.35	0.6

ANOVA results	*Source of variation*	*SS*	*df*	*MS*	*F*	*P-value*	*F critical*
Coal AN	B/G	0.07	2.00	0.003	0.003	0.99	3.35
	W/G	24.16	27.00	0.895			
Coal EM	B/G	0.00	1.00	0.00	0.00	0.97	4.41
	W/G	2.96	18.00	0.16			
Coal GS	B/G	0.001	1.00	0.001	0.01	0.95	4.41
	W/G	4.45	18.00	0.25			
Coal IN	B/G	0.003	1.00	0.003	0.01	0.93	4.41
	W/G	8.41	18.00	0.47			
Coal SF	B/G	0.00	1.00	0.001	0.002	0.97	4.41
	W/G	6.78	18.00	0.36			

B/G - Between groups; W/G - Within groups

4.4.2. Coals tested at 50°C

Figure 19 illustrates the comparison of the two (2) SA coals tested at 50°C versus the computed mean sorption ($\bar{x}$) (results in mmol/g per coal sample.

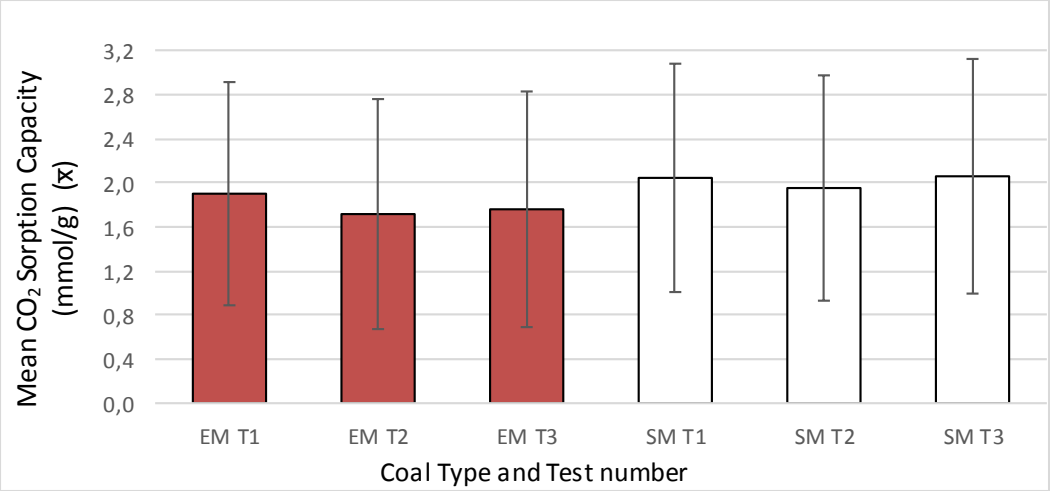

Figure 19. CO_2 sorption capacity comparison at 50°C using ANOVA results

Error bars which represent the calculated standard deviation (SD) show good repeatability was achieve for each coal type and test run done conducted. Table 7 summarizes the ANOVA

statistical data. For both coals tested the F statistic values range in the region of 0.03 – 0.09, which is less than the computed F critical value (3.35). This indicates that a good confidence level for repeat results, proving that the null hypothesis for these experiments is valid i.e. there is *not* a significant difference between the groups or data sets. The p-values computed, range from 0.92 – 0.97, showing excellent reproducibility of CO_2 sorption results for both these SA coals tested.

Table 7. Data summary and ANOVA results of coals tested at 50°C

Summary data			*Count (n)*	*Sum (Σ)*	*Mean ($\bar{x}$)*	*Variance (s^2)*	*Standard deviation (SD)*
Coal EM	TEST 1		10	19.0	1.90	1.02	1.0
	TEST 2		10	17.2	1.72	1.09	1.0
	TEST3		10	17.6	1.76	1.14	1.1
Coal SM	TEST 1		10	20.4	2.04	1.07	1.0
	TEST 2		10	19.5	1.95	1.04	1.0
	TEST3		10	20.6	2.06	1.13	1.1
ANOVA results	*Source of variation*	*SS*	*df*	*MS*	*F*	*P-value-*	*F critical*
Coal EM	B/G	0.19	2.00	0.09	0.09	0.92	3.35
	W/G	29.23	27.00	1.08			
Coal SM	B/G	0.07	2.00	0.03	0.03	0.97	3.35
	W/G	29.22	27.00	1.08			

B/G - Between groups; W/G - Within Groups

4.4.3. Coals tested at 60°C

Figure 20 illustrates the comparison of the two (2) SA coals tested at 60°C versus the computed mean sorption ($\bar{x}$) results in mmol/g per coal sample.

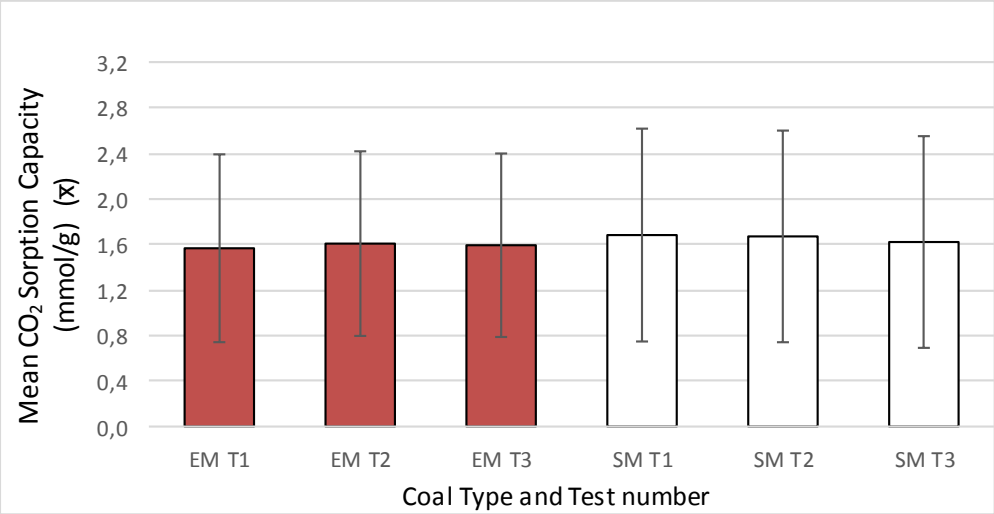

Figure 20. CO_2 sorption capacity comparison at 60°C using ANOVA results

Error bars which represent the calculated standard deviation (SD) show good repeatability was obtained for each coal type and test run conducted. Table 8 summarizes the ANOVA statistical data. For both coals tested the F statistic values are 0.01, which is less than the computed F critical value in the range of 3.35 -3.40. This indicates a good confidence level for these repeat results obtained in this study, proving that the null hypothesis for these experiments is valid i.e. there is *not* a significant difference between the groups or data sets. The p-values computed, are at 0.99, showing very good and acceptable reproducibility of the CO_2 sorption data set comparison of the repeat test results for both these SA coals, even at elevated temperatures.

Table 8. Data summary and ANOVA results of coals tested at 60°C

Summary data			*Count (n)*	*Sum (Σ)*	*Mean ($\bar{x}$)*	*Variance (s^2)*	*Standard deviation (SD)*
Coal EM	TEST 1		10	15.6	1.56	0.68	0.8
	TEST 2		10	16.1	1.60	0.66	0.8
	TEST3		10	16.0	1.59	0.65	0.8
Coal SM	TEST 1		10	15.1	1.68	0.87	0.9
	TEST 2		10	15.0	1.67	0.86	0.9
	TEST3		10	14.6	1.62	0.86	0.9
ANOVA results	*Source of variation*	*SS*	*df*	*MS*	*F*	*P-value-*	*F critical*
Coal EM	B/G	0.01	2.00	0.004	0.01	0.99	3.35
	W/G	17.87	27.00	0.66			
Coal SM	B/G	0.01	2.00	0.004	0.01	0.99	3.40
	W/G	17.87	27.00	0.66			

B/G - Between groups; W/G - Within roups

4.4.4. Summary of international published CO_2 sorption data comparison

Table 9 summarises some of the internationally published CO_2 sorption data. Reported here are only data that has been published in the units of milli mole per gram (mmol/gram) of adsorbed CO_2 as was the findings in this investigation. Other published data could not be compared as conversion to units of mmol/g cannot be undertaken due to unknown sample masses (g) used from the tests published.

Table 9. Summary of published data on CO_2 adsorption in coal (low and high pressure)

Publication	Coal type	Coal rank	Ash/ Mineral	Particle type	Test conditions		CO_2 adsorption capacity (mmol/g)
Shimada *et al.* [54]	Japanese (Akabira)	Bituminous rank B		powder	60 bar, 35°C		1.65
Busch *et al.* [15].	US (Argonne Premium)**	High & medium volatile C bituminous	Low – Medium	powder	73.8 bar, 22 °C		1.05 – 2.31
Ceglarska-Stefanska & Zarebska [55].	Polish	Hard coal B	Medium	powder	40 bar, 25°C,		22
		Hard coal M	Low				26
Bae & Bhatia [56]	Australian (Bowen Basin)	High vol. bit.	Medium	powder	200 bar	313K	0.033-0.06
						323K	0.034.-039
						333K	0.019-0.026
Soares *et al.* [57]	Brazilian	High volatile C bituminous	High	powder	<1 bar, 30°C 30°C		0.089-0.186
Goodman *et al.* [43]	US (Argonne Premium coals)	Low vol. bit.	Low	powder	150 bar, 55°C		0.44 – 9.07
		High vol. bit.	Medium				0.733-0.909
		Lignite	Low				0.68-1.476
Yu *et al.* [59]	Chinese (Qinshui Basin)		Low	powder	~60 bar, 28°C		0.97 – 1.3
Dutta *et al.* [24]	USA (Illinois)	High Volatile bituminous A	Medium	powder	50 bar, 28.6°C		0.929
		High Volatile bituminous B					0.998-1.198
Gruszkiewicz *et al.* [60]	US (Lower Pennsylvania)	Lack Warrior	Low – medium	powder	22-34 bar, 35 – 40°C		0.7-0.82
Gertenbach [61]	South Africa (Highveld, Waterberg)	Low Rank A-Medium Rank C	Low-medium	powder	50 bar, 35°C		0.3-1.5
Charriére *et al.* [62]	France	High Volatile Bituminous B	Low	powder	10 – 50 bar, 10 – 60 °C		0.34 – 1.55

Publication	Coal type	Coal rank	Ash/ Mineral	Particle type	Test conditions	CO_2 adsorption capacity (mmol/g)
Pone *et al.* [63]	USA (Kentucky)	Bituminous	Low	powder	69 bar,	1.17
Ozdemir & Schroeder [64]	Argonne Premium coals	Low Volatile B	Low	powder	30 bar, 22°C	1.25
		Med Volatile B	Medium			1.07
		High Volatile B	Low-high			1.17-1.65
		Sub bituminous	Low			1.97
		Lignite	Low			1.72
Li *et al.* [65]	Chinese	Anthracite	Low, Medium	powder	250 bar, 35°C	3.03
		Medium Volatile Bituminous				2.02
		Sub-bituminous				4.36
He *et al.* [66]	Korean	Anthracite	Medium –high	crushed	152 bar, 25 – 45°C	1.4 – 1.5
Zhang *et al.* [67]	Chinese	Bituminous	Low, Medium	powder	60 bar, 35°C	2.2, 1.0
			Low, Medium		120 bar, 50°C	1.6, 1.23
Pini *et al.* [68]	Swedish	Medium Volatile Bituminous	Low, medium	powder	190 bar, 45°C	0.75 – 1.31
Weniger *et al.* [69]	Silesia	Medium Volatile Bituminous	Low, medium	powder	55 bar, 20°C	1.07 – 1.36
Mabuza [40]	South Africa	High & medium volatile C bituminous	Medium – High	crushed	90 bar, 35°C	1.08 – 2.58
Ramasamy *et al.* [70]	Australian	Low, med, high volatile bituminous &, sub-bituminous	Medium	crushed	65 bar, 45.5°C	~1.0
Premlall K. current paper	South Africa	Anthracite, and Low, med, high volatile bituminous	Low-high	Crushed	~88 bar, 35°C	1.09 – 2.56
					~88 bar, 50°C	2.84 – 2.13
					~88 bar, 60°C	2.22 – 2.55

A good comparison in terms of calculated CO_2 sorption data can be seen from the previous reported sorption data acquired from other researchers using the same volumetric sorption method [15,43, 56-70], as compared to the CO_2 sorption data findings from the SA coals finding discussed in this paper using the volumetric sorption research equipment. It must be noted that most results presented are for powdered coals tested.

The comparison of CO_2 sorption results (mmol/g) from other researchers' studies, as presented in Table 9, shows good comparison and sits well for crushed SA samples and most certainly show a good assimilation and comparison thereof. Crushed samples used in this study give a very good indication that the compiled results can be well fitted using this experimental volumetric set up. It must be noted that crushed samples and powdered samples will show small discrepancies in absolute CO_2 sorption amounts (mmol/g), but this is acceptable as a given range per coal type and pressure injection is slightly varied in terms of the sorption test variables of test. Also to note that variation in sample mass, size and temperature and pressure variations are all to be taken into account when doing comparative review of all results.

5. Conclusions

In light of the construction of the only CO_2 sorption pressurized system in SA, the following conclusions regarding the validity of the system, can be drawn from this investigation and the

testing of the constructed sorption volumetric system from the varied CO_2 isothermal sorption isotherms, as well as from the analyzed ANOVA statistical assessment, demonstrated that the repeat test runs conducted at 35°C, 50°C and 60°C illustrated that exceptional equipment reliability and reproducibility of sorption data was achieved.

1. The overall sorption results for the five (5) South African coals tested at 35 and the two (2) evaluated at 50°C and 60°C, shows highly acceptable confidence levels for repeat results. The calculated p-values in all cases provide that the null hypothesis for these experiments is valid, i.e. there is *not* a significant difference between the groups or data sets that were re-produced. This is indicative of great reproducibility and consistency of the HPVSS during the test sorption experiments.
2. According to the set of sorption data that has been rigorously acquired and compared with the performance from other equipment reported in literature, it can be concluded that the data generated with this HPVSS are reliable and reproducible, thus affirming confidence in the designed and constructed high pressure volumetric sorption system.

References

[1] Blakemore E. 2017. Six irrefutable pieces of evidence that prove climate change is real. Popular Science. Online: https://www.popsci.com/evidence-climate-change-is-real. Accessed: May 2017.

[2] National aeronautics and space administration (NASA), 2018. Global Climate Change: Carbon dioxide latest measurements, [Online]: https://climate.nasa.gov/vital-signs/carbon-dioxide/; Accessed: August 2018.

[3] Centre for climate and energy solutions, Outcomes of the U.N. Climate Change Conference in Paris: 21st Session of the Conference of Parties to the United Nations Framework Convention on Climate Change (COP 21), December, 2016.

[4] van der Merwe, C. 2010. Energy and Climate change-policy and progress, ZEROCO2.

[5] National climate change policy, 2018. South Africa's Greenhouse Gas Emission Reduction System; [Online]: http://pmg-assets.s3-website-eu-west-1.amazonaws.com/180213enviro.pdf. Accessed: August 2018.

[6] IPCC, 2014: Summary for Policymakers. In: Climate Change 2014: Mitigation Climate Change Contribution of working group III to the Fifth Assessment Report of the Intergovernmental panel on Climate Change (eds Edenhofer, O., et al.), Cambridge, UK and New York, USA.

[7] Cloete M. 2010. Atlas on geological storage of carbon dioxide in South Africa (No. ISBN: 978-1-920226-24-4). Silverton, Pretoria, South Africa: Council for Geoscience VILJOEN, J., H, A,

[8] Stapelberg FDJ, Cloete M. 2010. Technical Report on the Geological Storage of Carbon Dioxide in South Africa. Silverton: Pretoria: Council for Geoscience.

[9] Jouber, JI, Grein CT, Bienstock D. Sorption of Methane in Moist Coal, Fuel, 1973; 52:181-185.

[10] Clarkson CR, Bustin RM. The effect of methane gas concentration, coal composition and pore structure upon gas transport in Canadian coals: implications for reservoir characterisation, International Coalbed Methane Symposium, Tuscaloosa, Al, Tulsa, May 1997, 12-16.

[11] Clarkson CR, Bustin RM. The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study. 1. Isotherms and pore volume distributions. Fuel, 1999; 78(11):1333-1344.

[12] Nodzenski A. Sorption and desorption of gases (CH_4, CO_2) on hard coal and active carbon at elevated pressures. Fuel, 1998; 77: 1243-1246.

[13] Laxminarayana C, Crosdale PJ. Role of coal type and rank on methane sorption characteristics of Bowen basin, Australia coals, International Journal of Coal Geology, 1999; 40: 309-325.

[14] Krooss BM, van Bergen F, Gensterblum Y, Siemons N, Pagnier HJM, David P. High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals. International Journal of Coal Geology, 2002; 51, 69-92.

[15] Busch A, Gensterblum Y, Krooss BM. Methane and CO_2 sorption and desorption measurements on dry Argonne premium coals: pure components and mixtures. International Journal of Coal Geology, 2003; 55, 205-224.

[16] Busch A, Gensterblum Y, Krooss BM. 2004. Methane and CO_2 sorption and desorption measurements on dry Argonne premium coals: pure components and mixtures. International Journal of Coal Geology, 2004; 45: 5.

[17] Busch A, Gensterblum Y, Krooss BM, Littke R. Methane and Carbon dioxide adsorption-diffusion experiments on coal: upscaling and modelling, International Journal of Coal Geology, 2004; 60: 151-168.
[18] Busch A, Gensterblum Y, Krooss BM, Siemons N. 2006. Investigation of high-pressure selective adsorption/desorption behaviour of CO_2 and CH_4 on coals: An experimental study, International Journal of Coal Geology, 2006; 66: 53-68.
[19] Busch A, Krooss BM. Molecular concept and experimental evidence of competitive adsorption of H_2O, CO_2 and CH_4 on organic material, Fuel, 2014; 115: 581–588.
[20] Belmabkhout Y, Frère M, de Weireld G. High-Pressure adsorption measurement. A comparative study of the volumetric and gravimetric methods. Measurement Science and Technology, 2004; 15: 848-858.
[21] Harpalani S, Prusty BK, Dutta P. Methane/CO_2 sorption modeling for coalbed methane production and CO_2 sequestration. Energy & Fuel; 2006; 20: 1591-1599.
[22] Siemons N, Busch A. Measurement and interpretation of supercritical CO_2 sorption on various coals, International Journal of Coal Geology, 2007; 69: 229-242.
[23] Zarębska K, Ceglarska-Stefańska G. The change in effective stress associated with swelling during carbon dioxide sequestration on natural gas recovery, International Journal of Coal Geology, 2008; 74: 167-174.
[24] Dutta P, Harpalani S, Prusty B., Modeling of CO_2 sorption in coal. Fuel, 2008; 87: 2023-2036.
[25] Dutta P, Bhowmik S, Das S. Methane and carbon dioxide sorption on a set of coals from India, International Journal of Coal Geology, 2011; 85: 289-299.
[26] Masterlez M, Gluskoter H, Rupp J. Carbon dioxide and methane sorption in high volatile bituminous coals from Indiana, USA, International Journal Coal of Geology, 2012; 60: 43-56.
[27] Merkel A, Gensterblum Y, Krooss BM, Amann A. Competitive sorption of CH_4, CO_2 and H_2O on natural coals of different rank, International Journal of Coal Geology, 2015; 150-151: 181-192.
[28] Li Z, Liu D, Cai Y, Shi Y. Investigation of methane diffusion in low-rank coals by a multiporous diffusion model, Journal of Gas Science and Engineering, 2016; 33: 97-107.
[29] Premlall K, Mabuza M, Wagner N. Evaluating CO_2 Sorption Capacity of a Number of South African (SA) Coal Types: Comparative Study of the Different Coal Properties at Incremental Pressures up to Supercritical Pressures. Energy Procedia, 2014; 51**,** 299-307.
[30] Mabuza M, Premlall K. Assessing Impure CO_2 Adsorption Capacity on Selected South African Coals: Comparative Study Using Low and High Concentrated Simulated Flue Gases. Energy Procedia, 2014; 51**,** 308-315.
[31] Lukhele KD, Premlall K, Shongwe M, Mabuza M, Daramola M. O. Effect of SO_2 co-feeding on CO_2 adsorption capacity of South African coals during CO_2 sequestration. Pet Coal, 2017; 59**,** 177-186.
[32] Mabuza M, Premlall K, Onyango MS, Daramola MO. 2018. Low-high temperature flue gas direct injection in south African bituminous and anthracite coals: sorption capacity assessment, Current Science, 2018; 115(4): 682-691.
[33] Premlall K, Wagner NJ. Evaluating Sorption capacity of a myriad of South African Coal types: Comparative Study of Sub-critical to Supercritical pressures, ICCS&T: International Conference on Clean Coal Technology, 29th September – 3rd October 2013, Penn Stater Hotel, Pennsylvania State University, USA.
[34] Premlall K, Wagner NJ. Laboratory experiments to determine best potential for cyclic supercritical CO_2 injections in SA coals to evaluate CH_4 desorption for ECBM potential, ICCS&T (International Conference on Coal Science & Technology), Hosted by: Engineers Australia and IChemE, 27th September – 2nd October 2015, Melbourne, Australia.
[35] Shongwe MG,Premlall K. Adsorption of flue gas on in-situ temperature profile of coal seam depth, ICCS&T (International Conference on Coal Science & Technology), Hosted by: Engineers Australia and IChemE, 27th September – 2nd October 2015, Melbourne, Australia.
[36] Mabuza M, Premlall K. Sorption of industrial flue gases on South African coals for CO_2 storage: experimental study on laboraotory scale, APOEEC 2015 – 3rd African Public Officials Energy and Environment Conference and Workshop, 3 – 5 June 2015, St. Georges Hotel and Convention Centre, Hosted by CEEP (Centre for Electric Energy and Power), Tshwane University of Technology Pretoria, South Africa. Proceedings ISBN: 978-0-620-65945-1.
[37] Premlall K, Wagner NJ. Feasibility of continued cyclic supercritical CO_2 injection in SA coals to evaluate CH_4 desorption for ECBM potential, APOEEC 2015 – 3rd African Public Officials Energy

and Environment Conference and Workshop, 3 – 5 June 2015, St. Georges Hotel and Convention Centre, Hosted by CEEP (Centre for Electric Energy and Power), Tshwane University of Technology Pretoria, South Africa. Proceedings ISBN: 978-0-620-65945-1.

[38] He J, Shi Y, Ahn S, Kang JW, Lee C-H. Adsorption and Desorption of CO_2 on Korean Coal under Subcritical to Supercritical Conditions. The Journal of Physical Chemistry B, 2010; 114**,** 4854-4861.

[39] Ozdemir E. Chemistry of the adsorption of carbon dioxide by Argonne Premium coals and a model to simulate CO_2 sequestration in coal. PhD, University of Pittsburgh 2004.

[40] Mabuza MM. 2013. Evaluating the adsorption capacity of supercritical carbon dioxide on South African coals using a simulated flue gas, Magister Technologiae, Tshwane University of Technology, Pretoria, South Africa.

[41] Day S, Sakurovs R, Weir S. Supercritical gas sorption on moist coals, International Journal of Coal Geology, 2008; 74(3-4): 203-214.

[42] Goodman AL, Busch A, Duffy GJ, Fitzgerald JE, Gasem KAM, Gensterblum Y, Krooss BM, Levy, J, Ozdemir E, Pan Z, Robinson RL, Schroeder K, Sudibandriyo M, White CM. 2004. An Interlaboratory Comparison of CO_2 Isotherms Measured on Argonne Premium Coal Samples. Energy & Fuels, 2004; 18: 1175-1182.

[43] Goodman AL, Busch M, Bustin L, Chikatamarla S, Day GJ, Duffy JE, Fitzgerald JE, Gasem KAM, Gensterblum Y, Hartman C, Jing C, Krooss BM, Mohammed ST, Pratt T, Robinson RL, Romankov V, Sakurovs R, Schroeder K, White CM. Inter-laboratory comparison II: CO_2 isotherms measured on moisture-equilibrated Argonne premium coals at 55 ^{0}C and up to 15 MPa, International Journal of Coal Geology, 2007; 72(3-4): 153 – 164.

[44] Gumma S, Talu O. Gibbs Dividing Surface and Helium Adsorption. Adsorption, 2003; 9:17-28.

[45] Sudibandriyo M. A Simple Technique for Surface Area Determination Through Supercritical CO_2 Adsorption. Makara of Technology Series, 2010; 14(1):1-6.

[46] McCarty RD Thermophysical properties of helium-4 from 2 to 1500 K with pressures to 1000 atmosphere. NBS Technical note 631. US Department of Commerce 1972.

[47] Hidnert P, Peffer EL. Density of Solids and Liquids. USA: Washington: United States Department of Commerce 1950.

[48] Charriére D, Pokryszka Z, Behra P. Effect of pressure and temperature on diffusion of CO_2 and CH_4 into coal from the Lorraine basin (France). International Journal of Coal Geology. 2010; 81: 373-380.

[49] Qing-Ling Z. Adsorption mechanism of different coal ranks under variable temperature and pressure conditions. Journal of China University of Mining and Technology, 2008; 18(3):395-400.

[50] Oldenburg C. Joule-Thomson Cooling Due to CO_2 Injection into Natural Gas Reservoirs, Energy Conversion and Management, 2007; 48: 1808-1815.

[51] NIST. 2016. National Institute of Standards and Technology-NIST Chemistry WebBook [Online]. Available: https://webbook.nist.gov/chemistry/#Search [Accessed]: 23 May 2018.

[52] Span R, Wagner W. 1996. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. Journal of Physical and Chemical Reference Data, 25**,** 1509-1596.

[53] Kim HJ, Sh, Y, He J, Lee H-H, Lee C-H. Adsorption characteristics of CO_2 and CH_4 on dry and wet coal from subcritical to supercritical conditions. Chemical Engineering Journal, 2011; 171**,** 45-53.

[54] Corder GW, Foreman DI. 2009. Nonparametric Statistics for Non-Statisticians. Hoboken: John Wiley & Sons. pp. 99–105. ISBN 9780470454619.

[55] Shimada S, Li H, Oshima Y, Adachi K. Displacement behaviour of CH_4 adsorbed on coals by injecting pure CO_2, N_2 and CO_2-N_2 mixture, Environmental Geology, 2005; 49: 44-52.

[56] Ceglarska-Stefańska G, Zarębska K. Sorption of carbon dioxide-methane mixtures, International Journal of Coal Geology, 2008; 62: 211-222.

[57] Bae JS, Bhatia SK, Rudolph V, Massarotto P. 2009. Pore Accessibility of Methane and Carbon Dioxide in Coals, Energy & Fuels, 2009; 23-3319-3327.

[58] Soares JL, Oberziner ALB, José HJ, Rodrigues AE, Moreira RFPM. Carbon dioxide adsorption in Brazilian coals, Fuels, 2007 ; 21: 209-215.

[59] Jessen K, Tang G-Q, Kovscek AR. Laboratory and Simulation investigation of enhanced coalbed methane Recovery by gas injection, Transport in Porous Media, 2008; 73(2): 141-159.

[60] Gruszkiewicz MS, Naney MT, Blencoe JG, Cole DR, Pashin JC, Carroll RE. Adsorption kinetics of CO_2, CH_4, and their equimolar mixture on coal from the Black Warrior, West-Central Alabama, International Journal of Coal Geology, 2009; 77: 23-33.
[61] Gertenbach RM. Methane and Carbon Dioxide sorption studies on South African coals, MSc Dissertation, University of Stellenbosch 2009.
[62] Charriére D, Pokryszka Z, Behra P. Effect of pressure and temperature on diffusion of CO_2 and CH_4 into coal from the Lorraine basin (France). International Journal of Coal Geology.2009; 81:373-380.
[63] Pone JDN, Halleck PM, Mathews JP. Sorption capacity and sorption kinetic measurements of CO_2 and CH_4 in confined and unconfined bituminous coal. Energy & Fuels, 2009; 23: 4688-4695.
[64] Ozdemir E, Schroeder K. Effect of Moisture on Adsorption Isotherms and Capacities of CO_2 on coals, Energy & Fuels, 2009; 23: 2821-2831.
[65] Li K. Carbon Capture by Adsorption. Cooperative Research Centre for Greenhouse Gas Technology (CO_2CRC): Monash University 2011.
[66] He J, Shi Y, Ahn S, Kang JW. Adsorption and Desorption of CO_2 on Korean Coal under Subcritical to Supercritical Conditions. The Journal of Physical Chemistry B, 2010; 114(14):4854-4861.
[67] Zhang D, Cui YJ, Li SG. Adsorption and diffusion behaviours of methane and carbon dioxide on various rank coals. Journal of Chinese Coal Society, 2011; 10:1693–8.
[68] Pini R, Ottiger S, Burlini L, Storti G, Mazzotti M. Sorption of carbon dioxide, methane and nitrogen in dry coals at high pressure and moderate temperature. International Journal of Greenhouse Gas Control, 2012; 4(1):90–101.
[69] Weniger P, Franců J, Hemza P, Krooss BM. Investigations on the methane and carbon dioxide sorption capacity of coals from the SW Upper Silesian Coal Basin, Czech Republic. International Journal of Coal Geology, 2012; 93(0):23-39.
[70] Ramasamy S, Sripada PP, Khan MM, Tian S, Trivedi J, Gupta R. Adsorption behaviour of CO_2 in Coal and Coal Char, Energy & Fuels, 2014; 28, 5241-5251.

To whom correspondence should be addressed: Dr. K. Premlall, Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa, 0001; Premlallk@tut.ac.za